

Correlation of secondary organic aerosol with odd-oxygen in megacity outflow

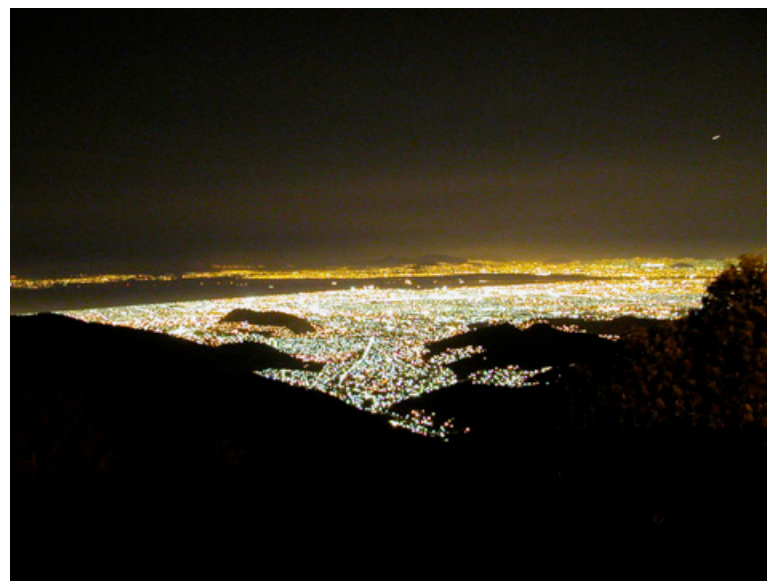
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Ingrid Ulbrich, Peter DeCarlo, Allison Aiken, Jose Jimenez, Dubey
Manvendra, Doug Worsnop, Charles Kolb and Luisa Molina

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Volkamer, Rafael Ramos, Armando Retama, Gustavo Sosa, Ana
Patricia

many MILAGRO Platforms - this analysis based on T0,
PTP and Santa Ana datasets - DE-FGO2-05ER63982

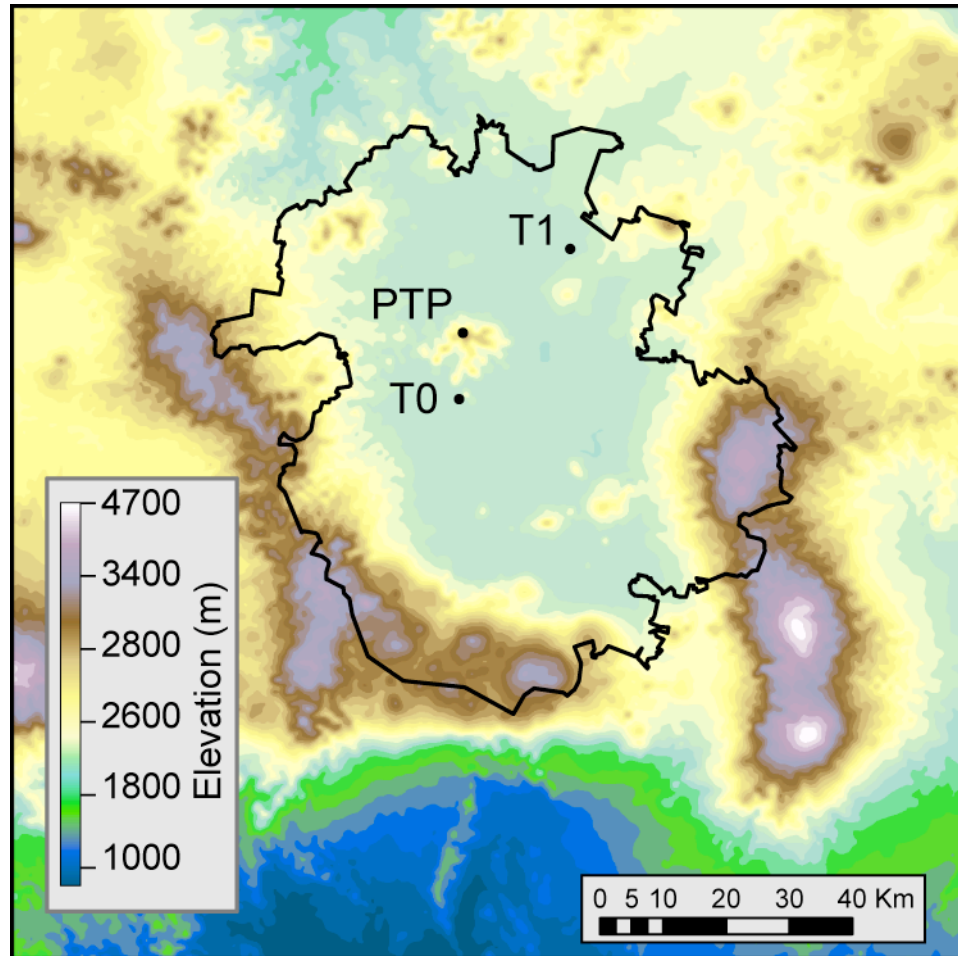


Photos by Berk Knighton



Mobile Laboratory housed various instruments for gas-phase and particulate characterization. Most were *online* sampling.

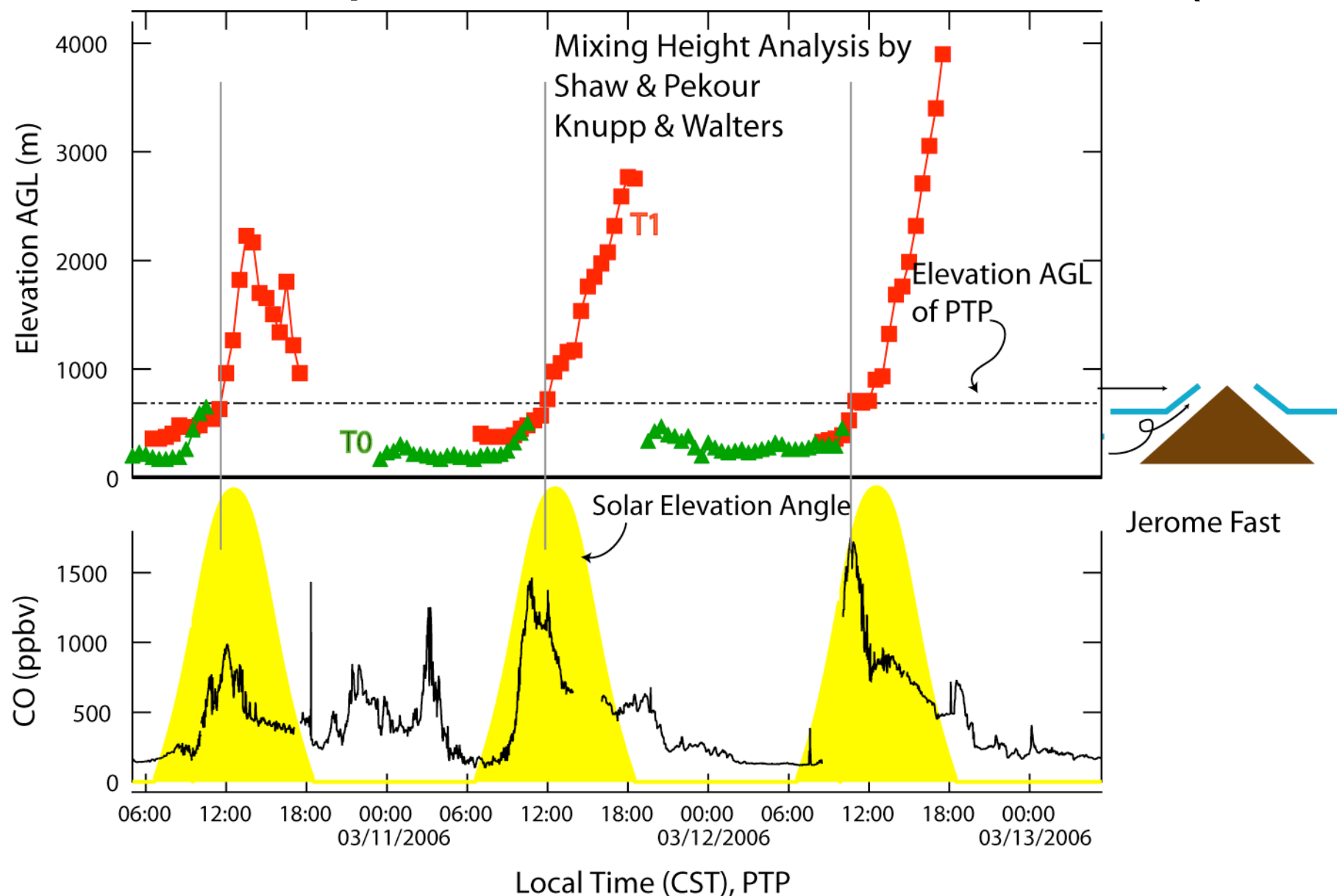
Topography of the Mexico City Metropolitan Area.



The site labeled “PTP” is an elevated location within the defined city limits.

Like T-1/2

Site Description Pico de Tres Padres (PTP)



Anthropogenic Organic Aerosol

Secondary organic aerosol has been observed to increase rapidly in urban outflow relative to CO

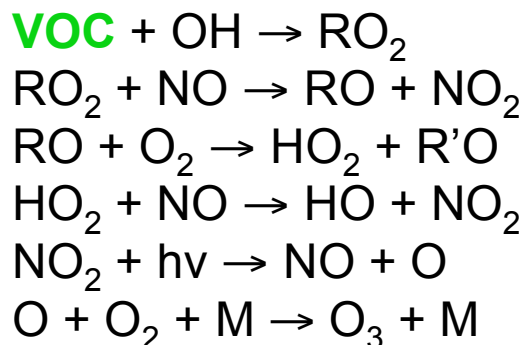
de Gouw, et al. 2005; Kleinman et al. 2006

Observed rates of SOA production in urban atmospheres are greater than current photochemical models predict

Volkamer et al. 2006

Ozone and SOA production in urban air

O₃ formation:



SOA formation:



Condensation of low-volatility
organic species

Pankow and Seinfeld, 2001

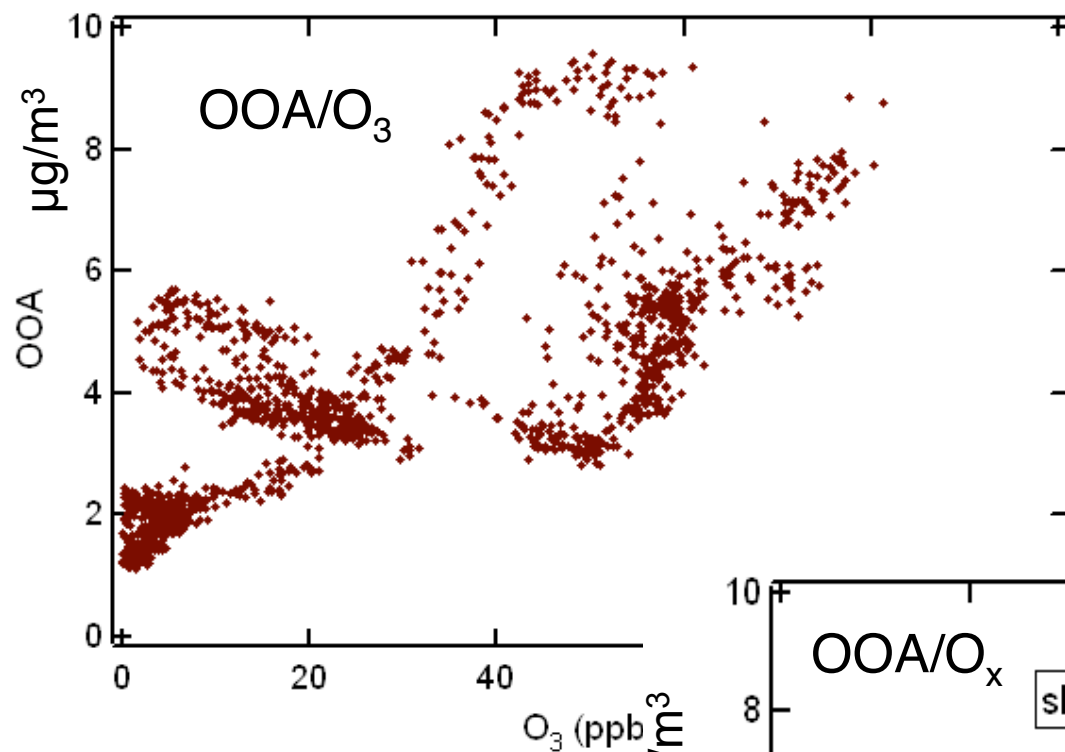
Chung and Seinfeld, 2002

Role of Aromatics

Odum et al. 1997, Ng et al. 2007

Same ingredients...

SOA and O₃ ought to be correlated

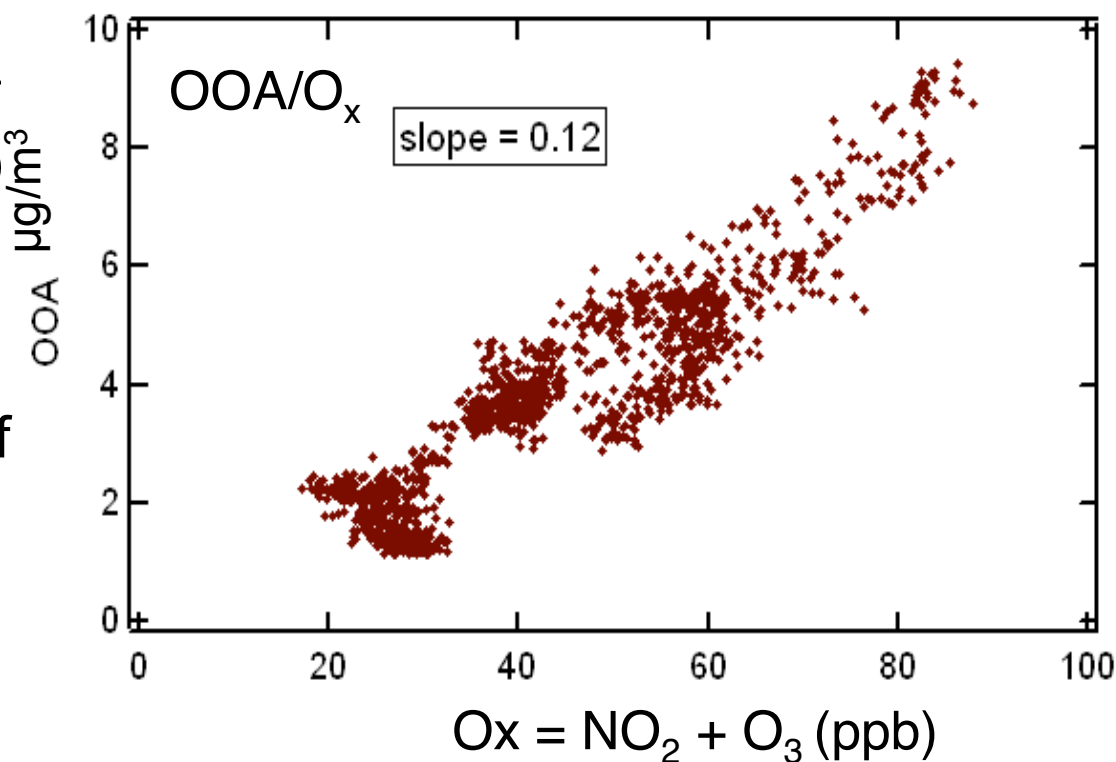


OOA vs O_3 or Ox?

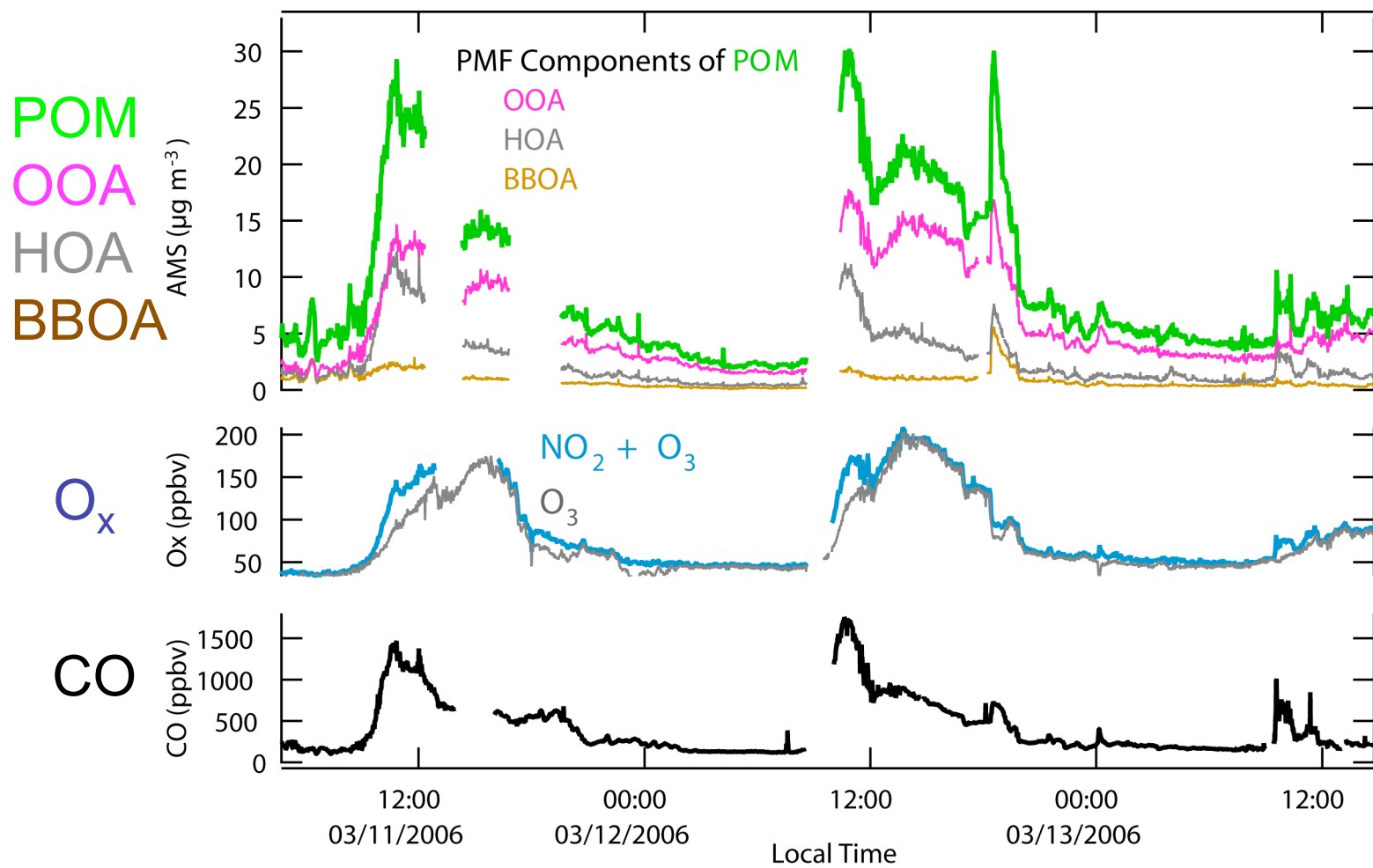
$$\text{Ox} = \text{NO}_2 + \text{O}_3$$

March 24, Santa Ana, 26 hrs

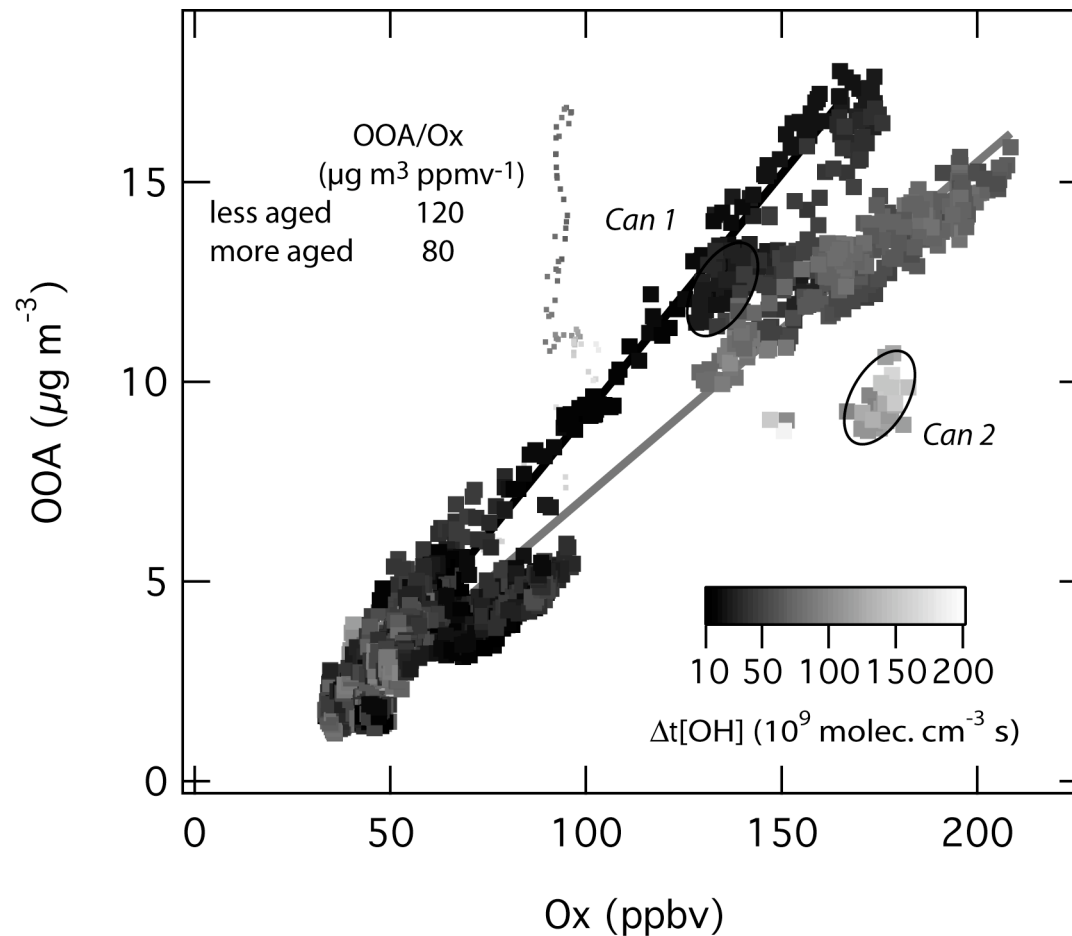
Ox is a more
conserved tracer of
photochemical
processing



Time Series of AMS and Gas-Phase Data at PTP



OOA vs Ox

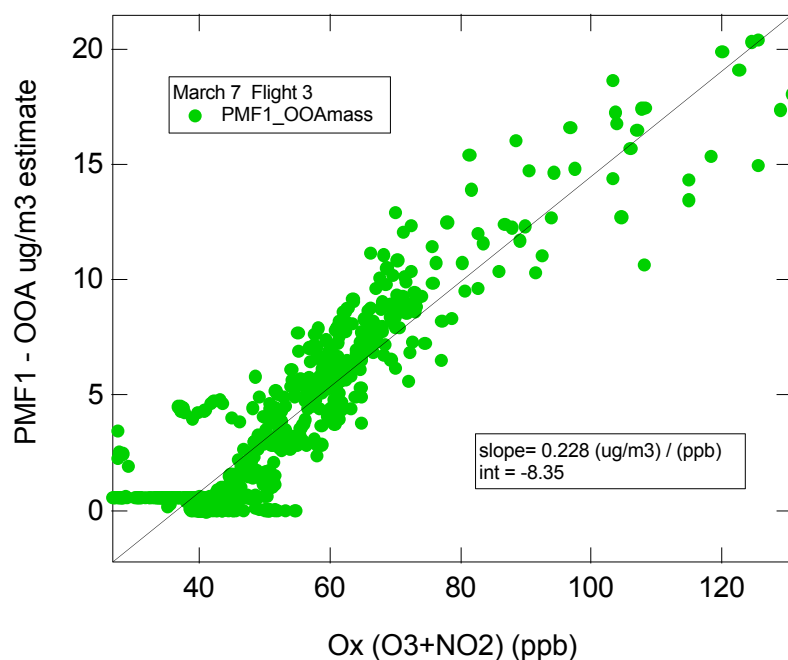


In earliest processing of the urban plume ~ 1 -10 hours, increases in OOA relative to Ox taper slightly

G1 Data - Preliminary OOA vs Ox

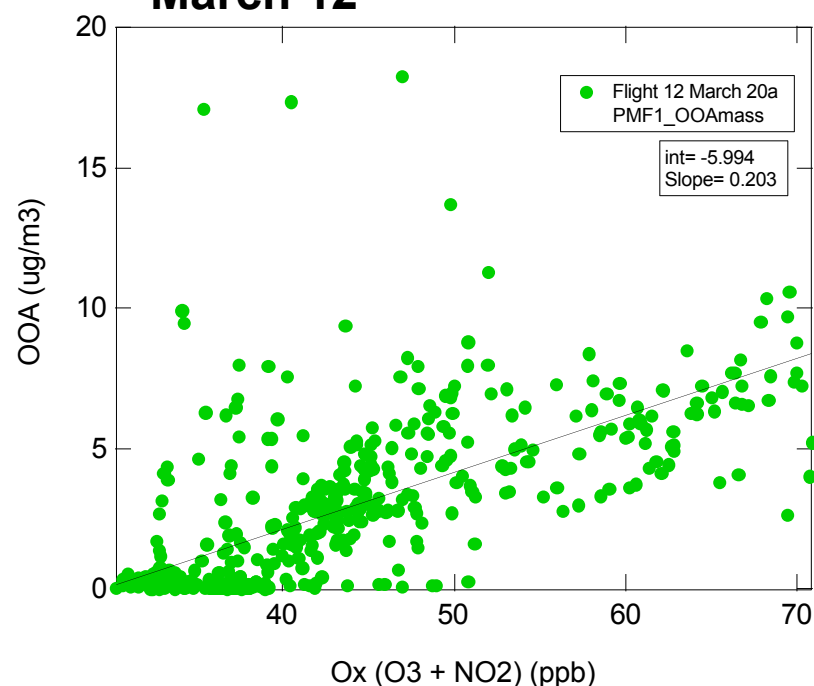
Springston, Jayne & Wood

March 7



Slope = 170 ug/m3 / ppm

March 12



Slope = 150 ug/m3 / ppm

Slopes (AMS loadings) are normalized to PTP pressure/temp

Final Notes

in urban outflow:

OOA to Ox ratio is proxy for $p(\text{SOA}) / p(\text{O}_3)$

*Applicability to Model Anthropogenic Aerosol - Jerome Fast

T1 to T0 inter-comparison

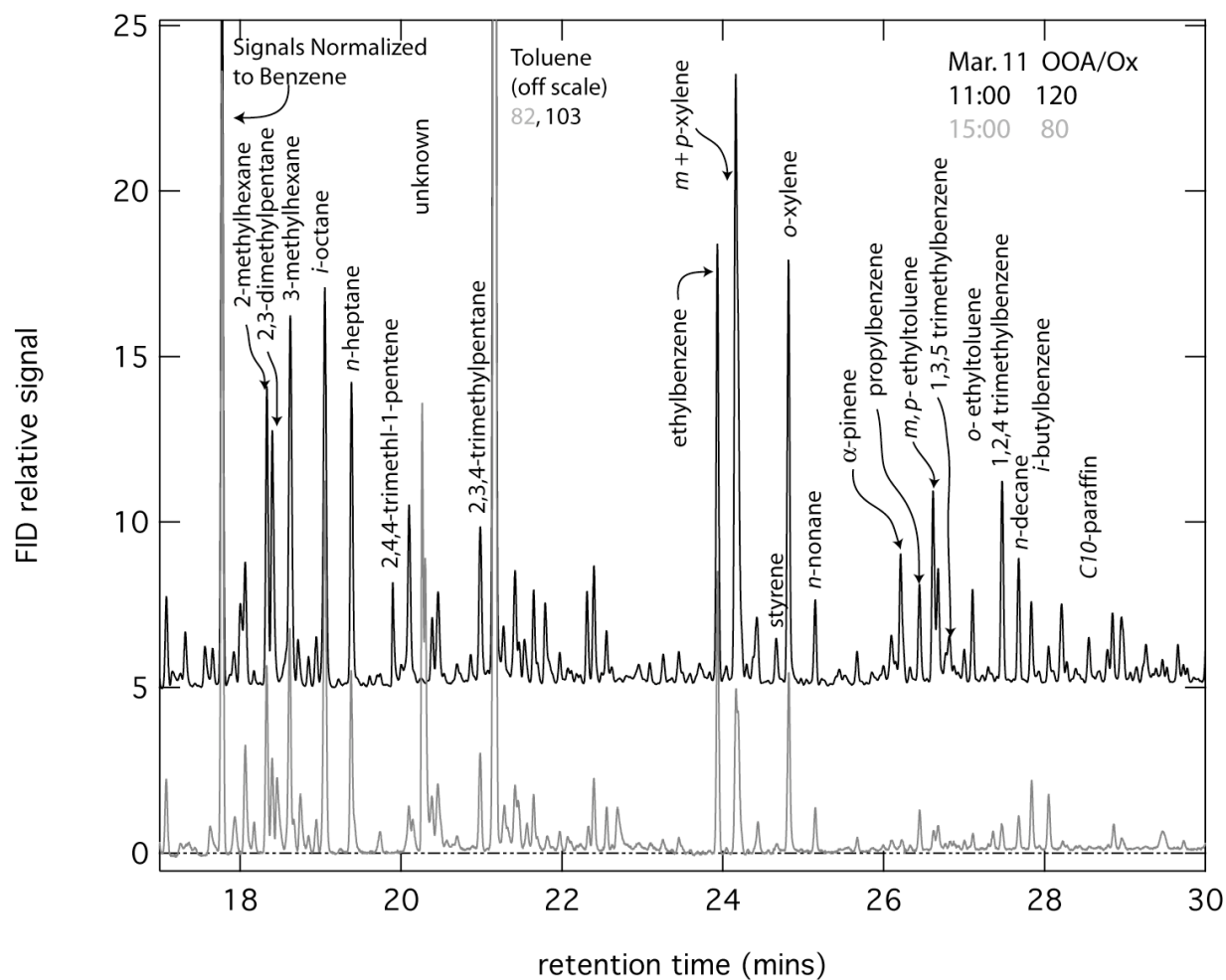
PTR and VOC measurements

Black Carbon to CO (variable)

Dubey Manvendra, Claudio Mazzoleni

Emission Ratios/Emission Inventory - Zavala

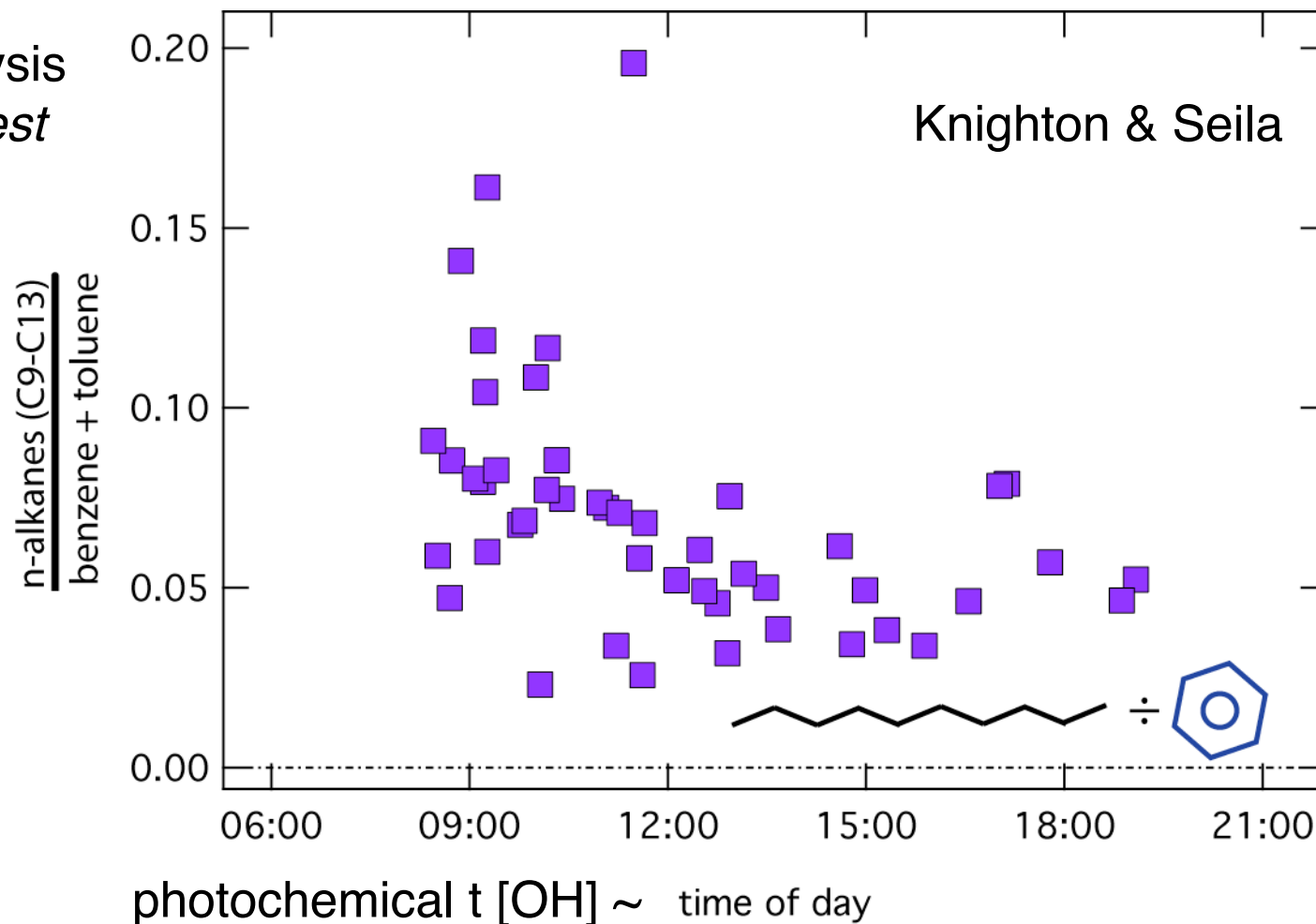
GC-FID Chromatograms for two time periods on 3/11 at PTP.



- The black trace is the chromatogram for the early morning canister sample and the grey trace is more photochemically processed air. The black less aged chromatogram has been offset 5 units for visual clarity. The two chromatograms have been normalized for dilution by equating the area of the benzene signal. Note that Toluene is off-scale for both chromatograms with the numbers 82 and 103 indicating the peak height in units of relative FID signal.

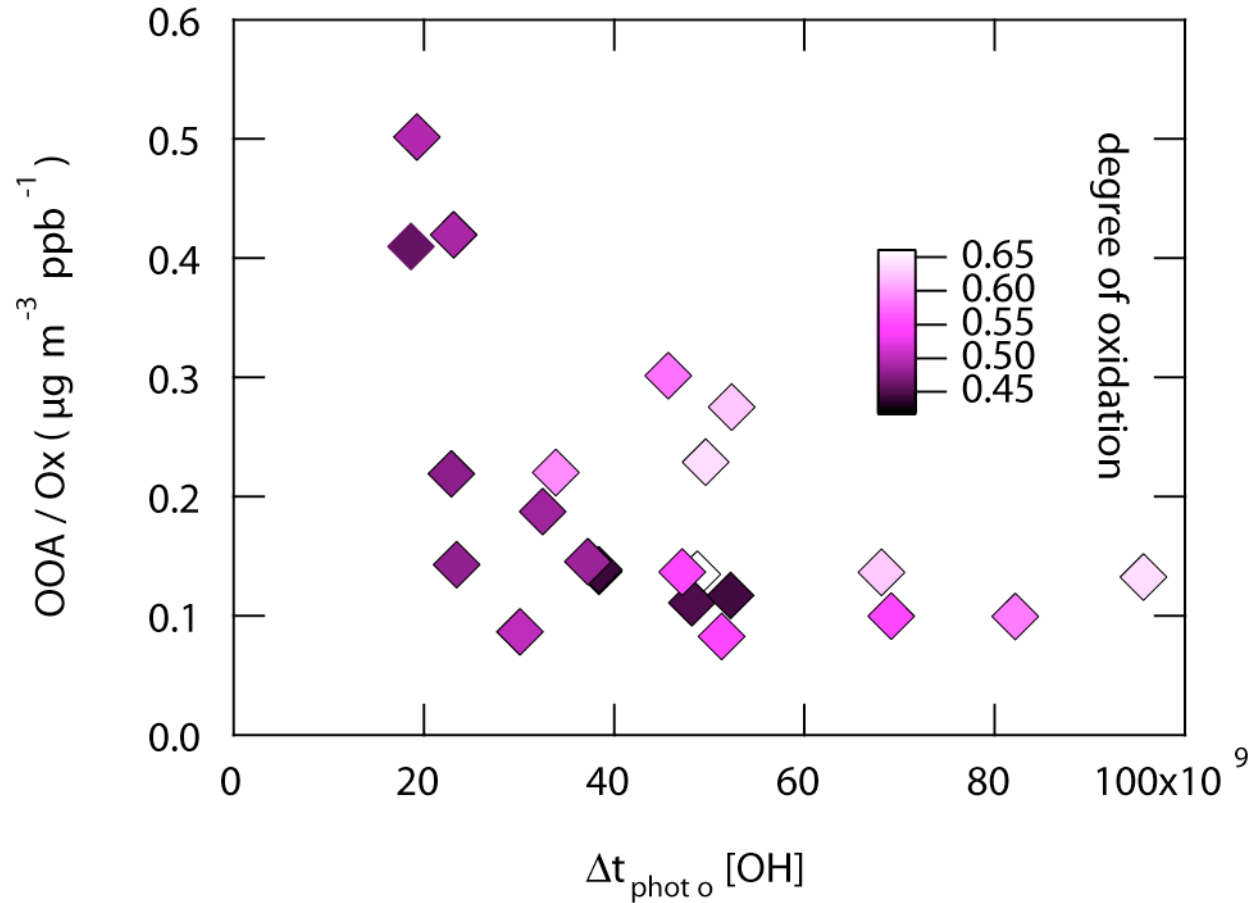
Diurnal change in VOC Mix at PTP

Canister Analysis
C9-C13 (*highest
reported*)



The potentially high yield n-alkanes, relative to aromatics taper in the afternoon

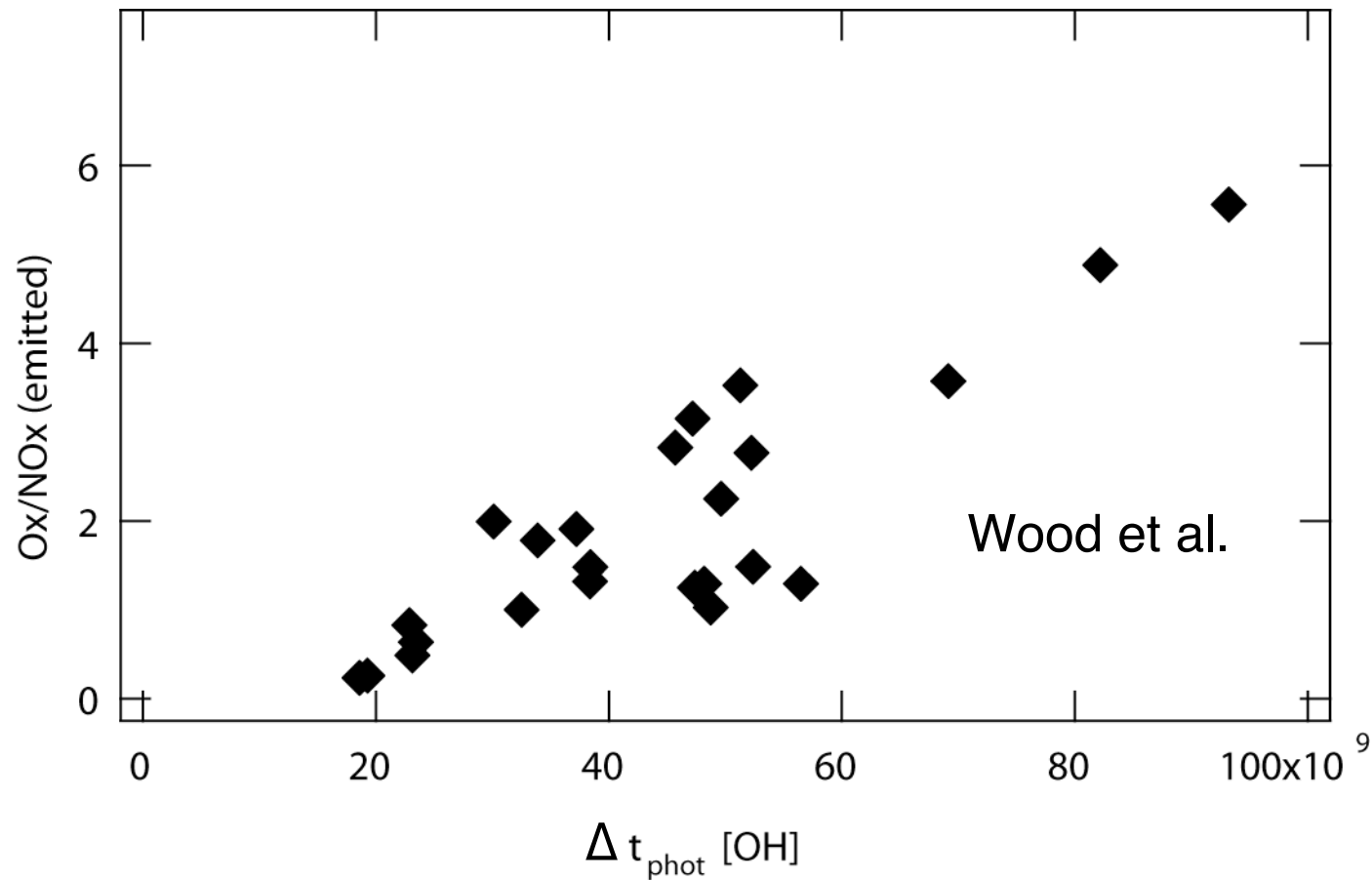
OOA/Ox



OOA/Ox decrease with photochemical processing

1. Fewer low volatility precursor
2. 2nd generation oxidation increases $p(\text{O}_3)$ relative to $p(\text{SOA})$

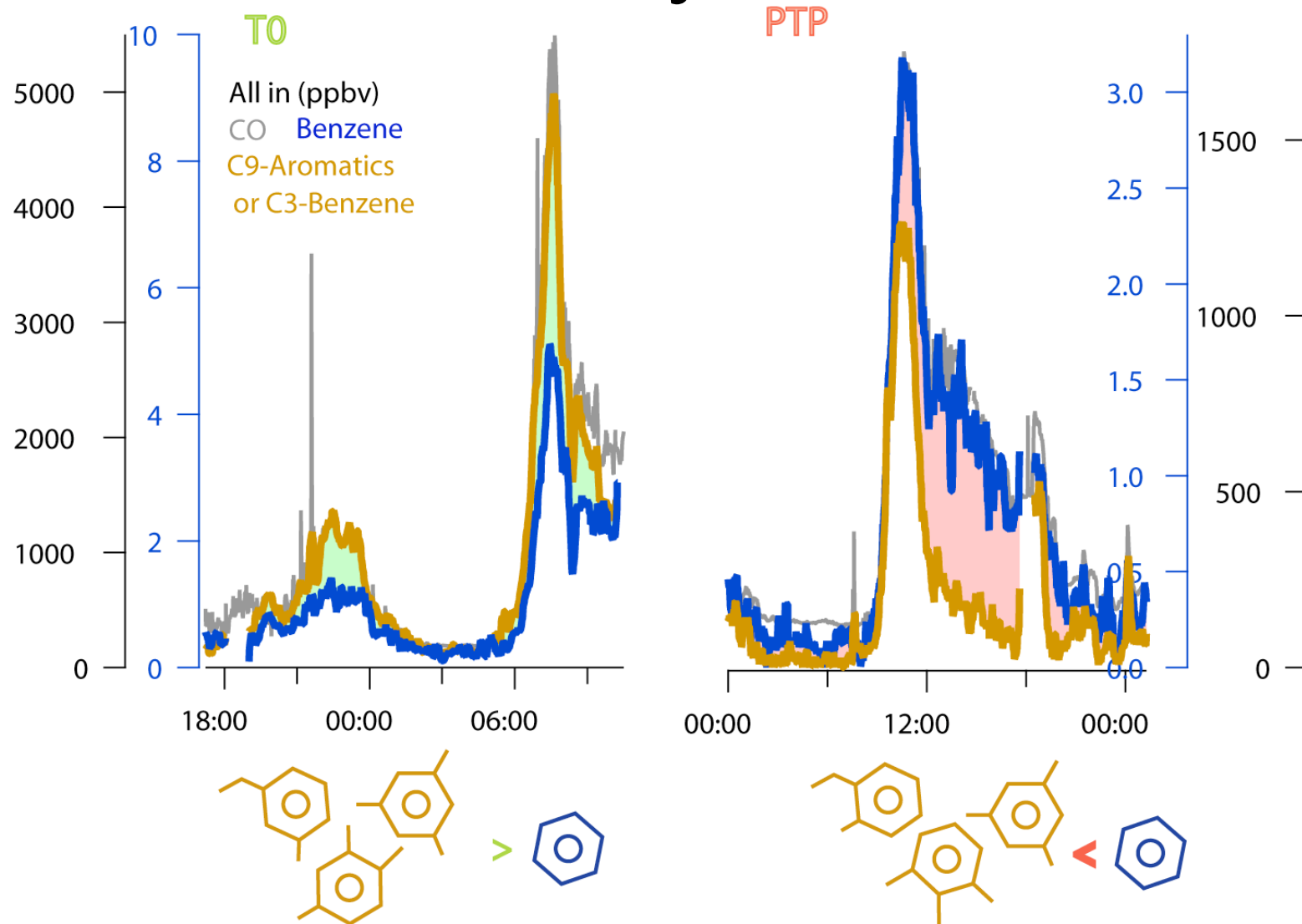
$$\text{O}_x/\text{NO}_x \sim [\text{OH}] \times \Delta t_{\text{photo}}$$



No O_x/NO_x plateau implies PTP is photochemically active

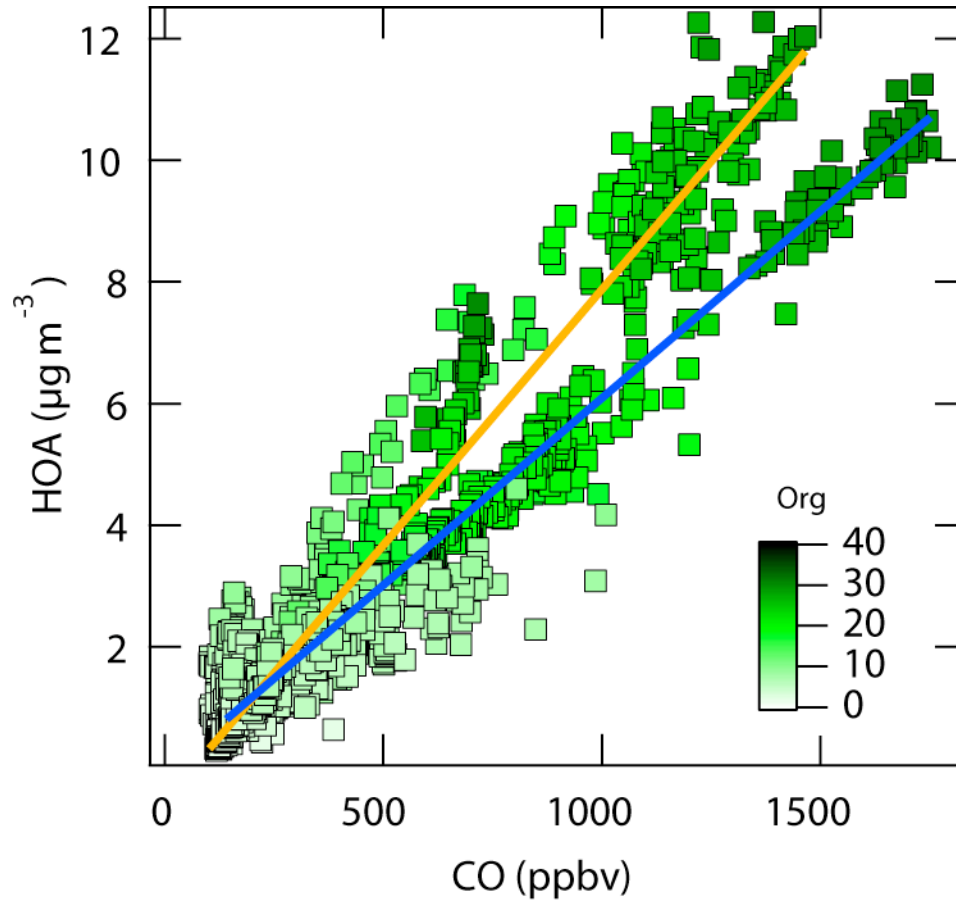
$\Delta t[\text{OH}]$
more to come...

Photochemistry - VOC Ratios



de Gouw, J. Roberts, McKeen, Liu

HOA correlates with CO



HOA/CO

3/11

$8.4 \mu\text{g m}^{-3} \text{ ppm}^{-1}$

3/12

$6.1 \mu\text{g m}^{-3} \text{ ppm}^{-1}$

Zhang et al.

Pittsburgh

$4.33 \mu\text{g m}^{-3} \text{ ppm}^{-1}$

POA/CO

de Gouw et al. $9.4 \mu\text{g m}^{-3} \text{ ppm}^{-1}$

Takegawa et al. $11 \mu\text{g m}^{-3} \text{ ppm}^{-1}$

EC carbon measurements correlate with HOA

Onasch & Mazzoleni

And on other days at PTP

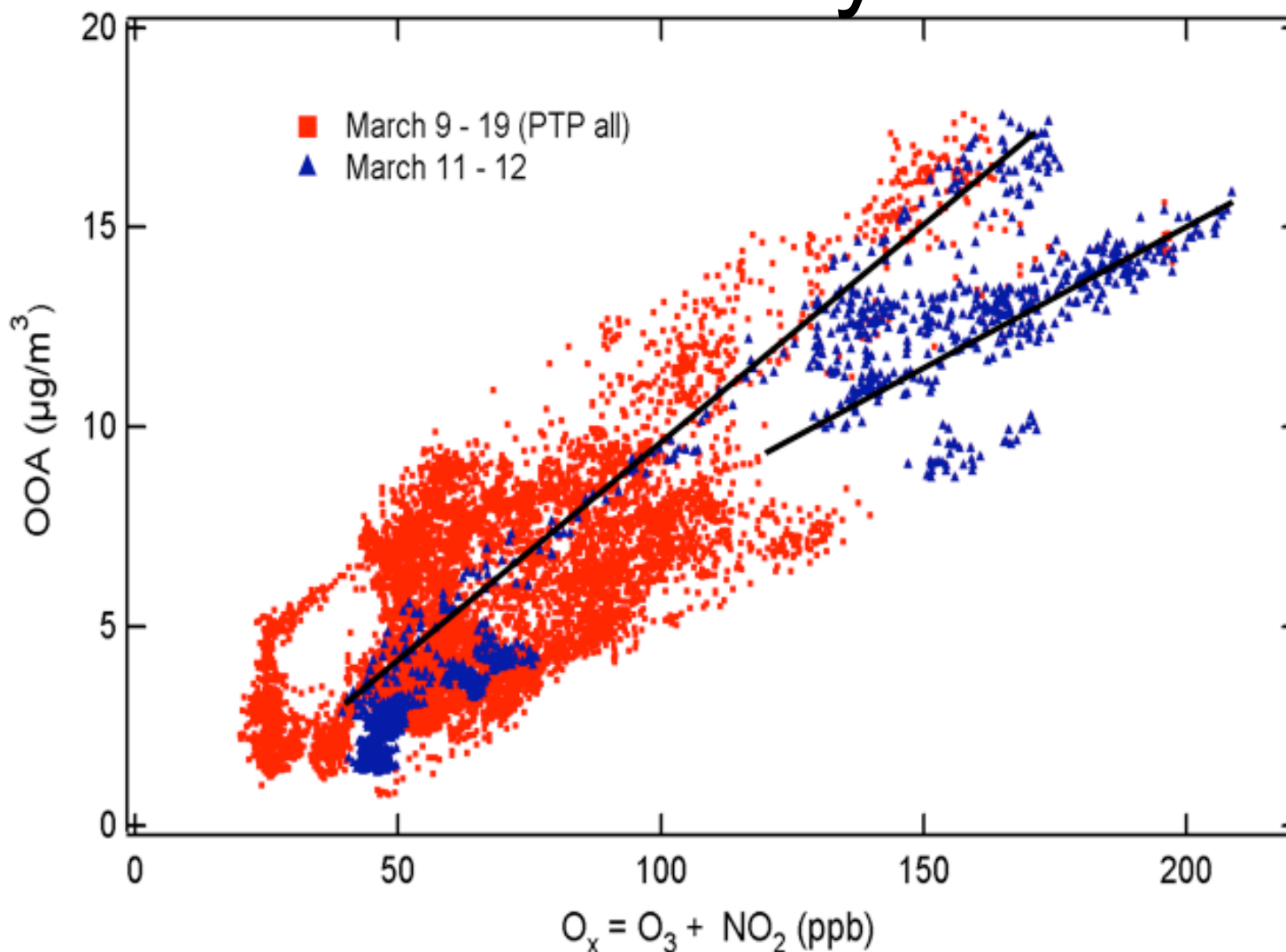
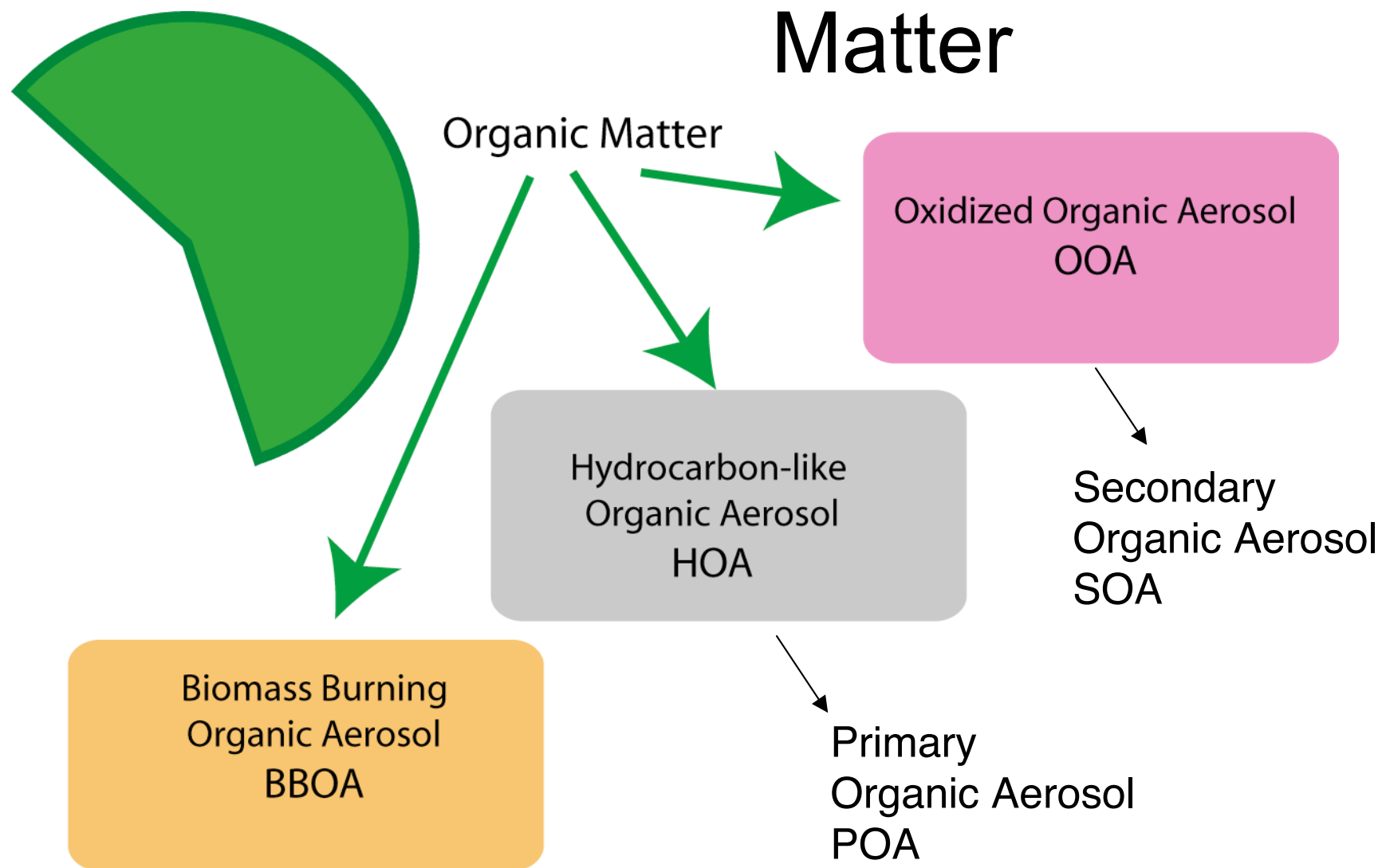


Figure 3.

Correlation of OOA with O_x for 9 days at the PTP site. The data from March 11 and 12 are shown in blue.

Further discussion of Organic Matter



Zhang et al., 2005, 2007; Lanz et al., 2006, Ulbrich et al.